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REVIEW

A comparative study of CO_2 sorption properties for different oxides

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Abstract It is essential to capture CO_2 from flue gas stream, which is considered as one of the prime reasons of global warming. Although various CO_2 capture technologies already exist, most of these techniques are still unfit to be employed at a large scale. In the past one decade, oxides have emerged as a strong candidate to capture CO_2 for post-, pre- and oxy-combustion conditions. Oxides combine with CO_2 present in the flue gas and form carbonate, which when heated regenerates the oxides and thus liberates almost pure stream of CO_2. The selection criteria for potential oxides entail their CO_2 capture capacity, absorption rate, thermal stability, regeneration heat, cost and structural properties. Thus, here, we review the technical merit of all the suitable oxides which can be used for CO_2 capture at any fossil fuel burning plants.

Keywords CO_2 capture technology · Carbonate · Capture capacity · Thermal stability · Regeneration heat · Structural properties

Introduction

The problem of carbon dioxide (CO_2) emission from various fossil fuel burning plants (such as power, steel, cement and gasifiers) has become an important issue that may tremendously affect our future survival. Carbon dioxide, one of the greenhouse gasses, contributes to the global warming effect once released into the atmosphere [1, 2]. CO_2 is thus far regarded as the most important contributor to global warming and accounts for 64 % of the increased greenhouse effect [3]. At present, there is ample scientific evidence to support the claim that global warming is human induced [4]. Many researchers believe that if such extensive use of fossil fuels continues for another 50 years, the CO_2 concentration will rise to 580 ppm, which would trigger a severe climate change.

The atmospheric concentration of CO_2 rose from 280 ppm in 1,800 to 397.8 in early 2014. Figure 1a presents the world energy-related CO_2 emissions. According to International Energy Outlook (IEO) 2013, the emission is projected to grow from 31.2 billion metric tons in 2010 to 45.5 billion metric tons in 2040. As expected, much of the growth is attributed to the developing countries (non-OECD). Non-OECD countries heavily rely on the supply of fossil fuels to meet their energy demand. The CO_2 emissions from the use of different fuel types such as coal, liquid fuels and natural gas are shown in Fig. 1b. Effluent emissions from coal use account for 44 % in 2010 and are projected to increase to 47 % in 2020–2030, before dropping marginally to 45 % in 2040. Liquid fuels have the slowest growth, resulting in an increment of only 3.5 billion metric tons of CO_2 from 2010 to 2040. The world consumption of natural gas is growing more rapidly than that of coal or liquid fuel. As natural gas has relatively low carbon intensity, its projected contribution to world energy-related CO_2 emissions is only 22 % in 2040.

Currently, most of the world energy requirement for transportation and heating (two-thirds of the primary energy demand) is satisfied through petroleum and natural gas. These two fuels are generally chosen due to the relative ease of transportation of liquid or gaseous forms. It is noteworthy that the combustion of hydrocarbon fuels for transportation and heating contributes over half of all

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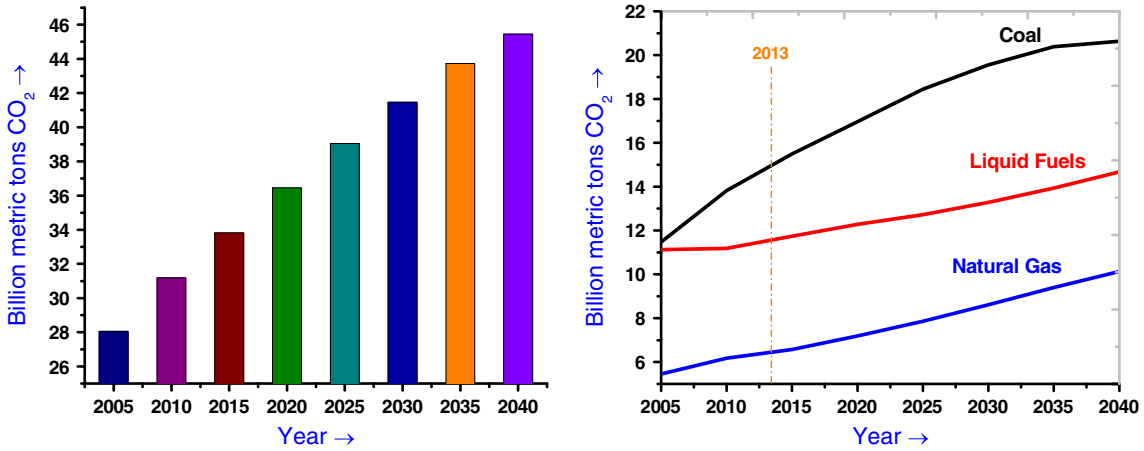

Fig. 1 World energy-related carbon dioxide emissions by **a** year and **b** fuel type

greenhouse gas emissions and a large fraction of air pollutant emissions. The current carbon emissions have to be reduced by at least a factor of three to maintain the CO_2 level in the atmosphere while meeting the ever-increasing global energy demand.

Therefore, it is essential to capture CO_2 from the industrial flue gas stream, one of the leading contributors of the anthropogenic gasses [5]. The development of carbon capture and sequestration (CCS) technologies can be seen as a viable solution to mitigate the vast carbon emission. The separation of a pure CO_2 stream, combined with a well-managed geological storage site, is being considered as a mitigation option for climate change. The CCS technologies could be applied using available technologies as many of the components in these systems are already in use. However, it is widely accepted that there is a large scope for cost reduction and energy efficiency improvements in CO_2 capture systems.

Currently, various CO_2 capture technologies exist including physical absorption [6, 7], chemical absorption [8, 9], adsorption [10] and membranes [11]. However, they are still far from being considered as a technologically viable solution. The obvious bottlenecks are the huge amount of flue gas which needs to be treated as well as low mass transfer rate during the processes. Among all the proposed techniques, chemical absorption using aqueous alkanolamine solutions is the most conventional way for CO_2 capture. But these amine-based solutions suffer severe drawbacks such as high energy consumption in regeneration process, high corrosive rate of equipment, essential pretreatment steps, large absorber volume and high sorbent cost. Because of these limitations of the chemical absorption techniques, an alternative way for post-, oxy- or pre-combustion CO_2 capture at fossil fuel burning power plants, mainly a solid adsorption/absorption method, can be proposed.

A schematic diagram on Fig. 2 is depicted to demonstrate the concept of cyclic CO_2 capture process by metal oxides. The metal oxides (MO), such as CaO and MgO, combine with CO_2 to form thermodynamically stable carbonates. Metal carbonates, when heated, liberate pure stream of CO_2 gas and regenerate the oxides. The combined use of exothermic carbonation reaction and endothermic regeneration reaction forms a cyclic process. Eventually, the generated pure CO_2 gas can either be sequestered underground or used for enhanced oil recovery [12]. In general, any metal oxides that can qualify for CO_2 capture application must be abundant in earth's crust, react with CO_2 at low temperature, require low regeneration energy, should have suitable reaction kinetics and must form a carbonate that is stable in the environment at ambient conditions. Porous oxides, namely alkali and alkaline-earth metals, have been reported as promising candidates for CO_2 capture. These metal oxides possess properties such as long durability, good mechanical strength, wide availability, and low cost since they are present as natural minerals and high CO_2 absorption capacity at moderate working temperatures [13–16]. In this study, we review the CO_2 capture capacity of these different potential oxides.

Selection criteria for metal oxides

Recently, researchers proposed a theoretical screening methodology to identify the most promising CO_2 sorbent candidates from the vast array of possible solid materials [17–19]. The methodology uses both the thermodynamic database searching with first principles density functional theory and phonon lattice dynamics calculations. The thermodynamic properties of solid materials are used for computing the thermodynamic reaction equilibrium

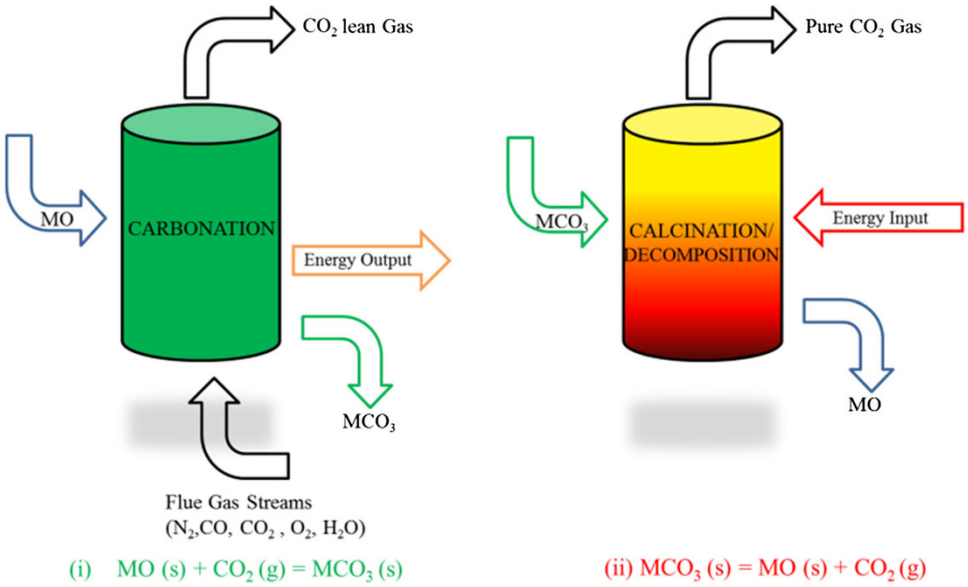

Fig. 2 Cyclic CO_2 capture process for metal oxides (MO) and metal carbonates (MCO_3)

properties of CO_2 absorption/desorption cycle based on the chemical potential and heat of reaction analysis. The selection is based on the pre- and post-combustion technologies and conditions in power plants. This includes only those solid materials that may be suitable as CO_2 sorbent candidates and further be considered for experimental validation, if they meet the following criteria: lead to lowering in energy cost for the capture and regeneration process and could operate at desired conditions of CO_2 pressure and temperature. Figure 3 illustrates the thermodynamic properties and CO_2 wt% absorbed by different metal oxides. However, the thermodynamic properties and CO_2 wt% absorbed by any sorbent could not be the only factors to select them for experimental studies. Various other important parameters such as availability or cost, regeneration temperature, kinetics, reversibility and durability must also be carefully considered before selecting any metal oxides for a large-scale application.

Based on the above figure, it can deduce that BeO has a favorable thermodynamics, but this system is not a viable candidate for CO_2 capture because of the health issues related to beryllium powder or dust. It should be noted that a high exothermic forward reaction ($MO(s) + CO_2$ (g) = $MCO_3(s)$) generally requires a large regeneration temperature for the oxide ($MCO_3(s) = MO$ (s) + CO_2 (g)). Also, a low CO_2 wt% (~40–50) will require a large amount of the solid materials to deal with a huge volume of flue gas stream at any fossil fuel burning plants. Thus, a high regeneration temperature and low CO_2 wt% can cause a vast energy or carbon emission penalty. Moreover, such oxides can eventually increase the electricity cost by a significant factor and thus may not be suitable for CO_2 capture at any plants.

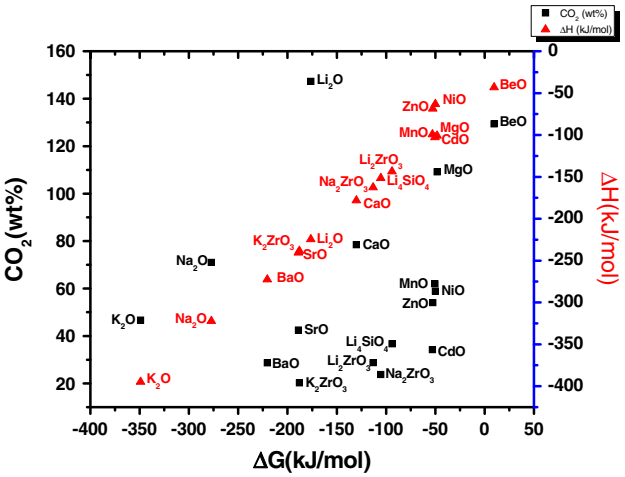

Fig. 3 Thermodynamic properties and CO_2 wt% for metal oxides MO(s) + CO_2 (g) = MCO_3(s) at 300 K

The turnover temperature represents the value above which sorbents cannot absorb CO_2 and the release of CO_2 begins. The flue gas conditions are different for pre- and post-combustion CO_2 capture at power plants. Under pre-combustion conditions, after water–gas shift reaction, the gas stream mainly contains CO_2, H_2O and H_2. The partial CO_2 pressure in this case is around 20–25 bar, and the temperature is about 300–350 °C. But for post-combustion conditions, the flue gas stream mainly contains CO_2 and N_2. In this case, the partial pressure of CO_2 is around 0.1–0.2 bar, while the temperature range can vary around 27–77 °C. The goal set up by the US Department of Energy is to capture at least 90 % CO_2 with an increase in the electricity cost of no more than 10 and 35 % for pre- and post-combustion technologies, respectively [20]. To minimize the energy consumption, the ideal sorbents should

work in the above-indicated pressure and temperature ranges to separate CO_2 from H_2. A list of turnover temperatures for different oxides can be found elsewhere [17–19].

Based on the above-discussed limitations, exclusively few oxides seem to be promising and thus chosen to study for the experimental validation. The two alkaline-earth metal oxides (such as CaO and MgO) draw the tremendous attention because of accessibility and favorable thermodynamics. Recently, lithium-, sodium- and potassium-based silicates or zirconates also gained interest due to their high CO_2 absorption capacity. Moreover, FeO can also be seen as a promising material for CO_2 capture at both power and non-power sectors (iron and steel industry). In the following sections, we review the experimental studies for the most promising CO_2 sorbent candidates.

Metal oxides

Alkali metal-based oxides

Lithium zirconate (Li_2ZrO_3)

The reaction between lithium carbonate (Li_2CO_3) and zirconium dioxide (ZrO_2) is well known to synthesize lithium zirconate (Li_2ZrO_3). However, the reverse reaction was not considered for CO_2 capture until 1998 [21]. Nakagawa and Ohashi first investigated the capture of CO_2 using Li_2ZrO_3 at high temperatures (400–600 °C) [21]. Li_2ZrO_3 has great potential because it has an excellent CO_2 sorption capacity (28 wt%) as well as a small volume change during the CO_2 sorption/desorption cycles [22]. The reaction (1) occurs mainly due to the Li ion mobility in the ceramics [23, 24]. As can be seen from Fig. 4, during CO_2 sorption, the Li ions diffuse from the core of the particles to the surface and react with CO_2 to form Li_2CO_3. The diffusion of CO_2 in the solid Li_2CO_3 is recognized as the rate-limiting step.

$$Li_2CO_3(s) + ZrO_2(s) \leftrightarrow Li_2ZrO_3(s) + CO_2(g) \quad \Delta H_{298K} = -160\,kJ/mol \tag{1}$$

The separation of CO_2 with aid of Li_2ZrO_3 works in a temperature range of 450–700 °C. The main advantage of this new material with respect to calcium-based absorbents is its unique thermal stability that allows achieving many absorption/regeneration cycles (over 20) without loss of capacity. Previous reports suggest that only 11–13 wt% change after absorption of CO_2 using Li_2ZrO_3 at 500–700 °C in more than an hour is possible. Thus, it is evident that Li_2ZrO_3 has extremely slow absorption kinetics, and hence, recently, the addition of dopants was proposed as a solution. Hence, the addition of dopants such as K_2CO_3 and Y_2O_3 to Li_2ZrO_3 could potentially accelerate its CO_2 sorption kinetics.

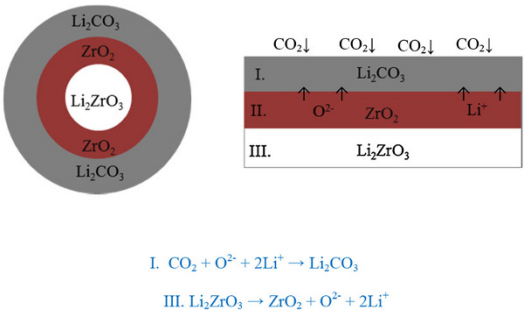

Fig. 4 Proposed mechanisms for CO_2 sorption on Li_2ZrO_3

In the case of the pure Li_2ZrO_3 (without K_2CO_3 additive), formation of an impervious shell of Li_2CO_3 on the surface leads to a residual unreactive Li_2ZrO_3 core (Fig. 4). This observation suggests that the diffusion resistance of CO_2 through the solid Li_2CO_3 surface layer is the rate-limiting step. At 500 °C, Li_2CO_3 and K_2CO_3 form a eutectic mixture. During the absorption process, the eutectic mixture helps to diffuse more CO_2 toward the inner unreacted particles [25]. K_2CO_3- and Li_2CO_3-containing Li_2ZrO_3 sample reacts with gaseous CO_2 at 500 °C to form an outer layer of a molten liquid and a solid interior ZrO_2 core. Consequently, CO_2 diffuses through the molten carbonate layer at a much faster rate. Such difference in CO_2 sorption rate of doped and undoped Li_2ZrO_3 can be partially attributed to the molten carbonate layer.

Another dopant, Y_2O_3, can improve the O^{-2} ionic diffusion in the ZrO_2 layer that is formed during the absorption. Unfortunately, Y_2O_3 failed to increase the CO_2 absorption kinetics of Li_2ZrO_3 [26]. Other findings reveal that solid solutions of lithium and potassium meta zirconates ($Li_{2-x}K_xZrO_3$) increase both the kinetics and CO_2 absorption capacity compared to undoped Li_2ZrO_3 [27]. In the same line, solid solutions of lithium and sodium zirconates were also explored [28]. It was concluded that the higher the Na content in the samples the faster the absorption kinetics. On the contrary, the higher the Li content in the mixture the faster the regeneration kinetics.

Lithium orthosilicate (Li_4SiO_4)

Lithium silicate-based (Li_4SiO_4) sorbent material has been considered as a promising candidate for high-temperature CO_2 removal in the recent times [29, 30]. Li_4SiO_4 could adsorb different concentrations of CO_2 in the temperature range of 450–700 °C, but it has relatively (compared to amine solutions) higher decomposition temperature (>800 °C). A high decomposition temperature implies that more heat input and costly equipment would be required to perform the process. However, compared to other solid sorbents such as CaO, the decomposition temperature is

low and thus less supply of energy will be needed [31]. As can be calculated from reaction (2), the theoretical CO_2 adsorption capacity of Li_4SiO_4 is 36.7 wt% ($\sim$8.34 mmol CO_2/g Li_4SiO_4).

$$Li_4SiO_4(s) + CO_2(g) \leftrightarrow Li_2SiO_3(s) + Li_2CO_3(s) \quad \Delta H_{298K} = -141.97\,kJ/mol \tag{2}$$

In a study, Wang et al. [32] reported an interesting way to synthesize Li_4SiO_4 using rice husk, which were calcined at 800 °C in the presence of Li_2CO_3. This material is ideally suited for CO_2 removal from synthesis gas (syngas) derived from gasification of carbonaceous fuels (coal, coke, natural gas, biomass, etc.) and is hence considered as a pre-combustion CO_2 sorbent.

Li_4SiO_4 has shown the ability to remove more than 90 % of the CO_2 from simulated syngas in both fixed-bed and fluidized-bed process configuration. The lithium silicate-based sorbent is highly effective at temperatures of 250–550 °C, pressures of 0–20 atm, CO_2 concentrations of 2–20 % and in the presence of contaminants such as hydrogen sulfide. Yamachui et al. [33] reported a carbonation yield of 87.2 % under 100 cm^3/min flow rate of pure CO_2. The water vapor plays a major role in increasing the CO_2 absorption rates of Li_4SiO_4. About 22–26 wt% (capacities of $\sim$5−6 mmol/g) were obtained using a gas stream containing about 15 % CO_2 and 10 % H_2O in N_2 at 550 °C [34]. Moreover, the sorbent has shown excellent regenerability and attrition resistance in thermal cycling tests. Recent analysis has shown that the lithium silicate-based sorbent has the capability not only to separate CO_2 from syngas, but also to promote the water–gas shift reaction [35]. It is reported that dopants such as Al, Fe, Na, K and Cs increase the CO_2 uptake of lithium orthosilicate [36, 37].

Researchers have attempted to improve the reaction kinetics of CO_2 adsorption by altering the synthesis routes [38]. The new methods are aimed at reducing the particle size of Li_4SiO_4. The experimental results reveal that a smaller particle size yields higher CO_2 adsorption efficiency and adsorption rate. Further studies focused on decreasing the precursor particle size [39] or choosing more sintering-resistant precursor to result in the smaller product grain size [40]. Similarly, based on the particle size effects on Li_4SiO_4, the reactivity of Li_4SiO_4 was modeled as a reaction of CO_2 at the solid surface followed by the rate-limiting diffusion of lithium [41].

A calculation based on the most optimistic assumptions illustrates that despite the fact that Li_4SiO_4-based absorbent demonstrates high CO_2 uptake capacity, it would be impractical to perform the process at the scale of a fixed-bed temperature swing process at a 500-MW coal-fired power plant [34]. However, efforts have been made to modify the Li_4SiO_4 synthesis methods such as solid-state reactions [30, 42], sol–gel method [38, 43], impregnated suspension [44], precipitation method [45], amorphous silica [40], Quartz [39], fly ashes [46], rice husk ashes [47] and diatomite [48].

Sodium zirconate (Na_2ZrO_3)

Sodium zirconate has gained attention due to its favorable thermodynamics and high theoretical CO_2 sorption capacity [23, 49, 50]. Na-based sorbents can be used as solid CO_2 acceptors at high temperatures. The use of sodium-based oxides is more economical than lithium-based oxides. Moreover, previous reports suggest that Na_2ZrO_3 can have a better reaction rate than the synthetic sorbents such as Li_2ZrO_3 and Li_4SiO_4 [51].

Na_2ZrO_3 has a lamellar structure, where sodium ions are located among the zirconate layers, which permits for sodium diffusion. The mechanism for CO_2 chemisorption on Na_2ZrO_3 has already been proposed. Initially, the surface of the alkaline ceramic particles reacts with CO_2 and forms carbonates on the periphery. Once the external layer of carbonate is completely formed, sodium atoms have to diffuse throughout this external carbonate shell to reach the surface and be able to react with CO_2.

$$Na_2ZrO_3(s) + CO_2(g) \leftrightarrow Na_2CO_3(s) + ZrO_2(s) \tag{3}$$

The maximum theoretical CO_2 absorption should correspond to an increase of weight equal to 23.75 wt%. The reaction (3) is controlled by two different processes—CO_2 absorption over the surface of Na_2ZrO_3 particles and sodium diffusion. Alcerreca-Corte et al. [52] performed the kinetic analysis for chemisorption of CO_2 on the Na_2ZrO_3 particles in the temperature range of 150–700 °C. A fast kinetics was observed between 550 and 700 °C. However, at low temperatures, kinetics was relatively low and was attributed to the sintering effect as well as diffusion problems. The optimum temperature for the reaction (3) was 600 °C. All the isotherms were fitted to a double exponential model. The activation energies for the CO_2 absorption and the diffusion of sodium were calculated to be 33.87 and 48.01 kJ/mol, respectively. Therefore, it was concluded that sodium diffusion is the limiting step of the process. Similarly, Jimenez et al. reported the CO_2 sorption kinetics of Na_2ZrO_3 at similar temperatures and $P_{CO_2} = 0.4$–0.8 atm. Contrary to previous study, the surface reaction is identified to be the rate-limiting step for the reaction and attributed to the fast CO_2 sorption kinetics of Na_2ZrO_3 [53].

In general, the addition of steam enhances the capture kinetics and also favors the regeneration. It is believed that the presence of steam increases the mobility of alkaline

ions and therefore accelerates the reactions. Therefore, several studies have been performed to evaluate the effect of steam addition on the CO_2 capture properties of Na_2ZrO_3 [54, 55]. One such study was performed by Santillán-Reyes et al. in the presence of water vapor and low temperature range (30–70 °C). They synthesized Na_2ZrO_3 by solid-state reaction using the reagents Na_2CO_3 and ZrO_2 in the molar ratio of 1.1:1.0, respectively. Further, the reaction mechanism of Na_2ZrO_3–CO_2–H_2O was proposed and illustrated in (4). Na_2ZrO_3 reacts with water vapor to produce hydroxyl species at the particle surfaces and then absorbs 2 mol of CO_2 and 1 mol of H_2O to eventually form $NaHCO_3$ and ZrO_2.

$$Na_2ZrO_3 \xrightarrow{H_2O} Na_2ZrO_{3\,\text{superficially hydroxylated}} \xrightarrow{2CO_2} 2NaHCO_3 + ZrO_2 \quad (4)$$

Na_2ZrO_3 was able to absorb 5.8 mmol/g of CO_2 (which has theoretical capacity is 10.8 mmol/g). Therefore, Na_2ZrO_3 can also be used as CO_2 sorbent at low temperatures and in the presence of water vapor. The reported absorption results for Na_2ZrO_3 are still higher than for other materials in the same temperature conditions ($\leq$6 mmol/g of material) [56].

Nanosized materials are expected to increase the CO_2 capture/regeneration rates due to their improved characteristics, such as high surface area and higher surface reactivity because of unsaturated bonds on their pristine surfaces [57–59]. Therefore, Zhao et al. synthesized nanosized Na_2ZrO_3 using a soft-chemical route starting with the formation of a complex from zirconoxy nitrate and sodium citrate, followed by highly exothermic reaction between citrate and nitrate during calcination in a controlled atmosphere [49]. It was found that much faster CO_2 capture rates can be achieved on the monoclinic Na_2ZrO_3 compared to the hexagonal one, even at a very low CO_2 pressure (0.025 bar). Thus, a higher CO_2 capture rate is obtained for nanosized Na_2ZrO_3 due to the dual effect of its crystal size and structure.

Moreover, the doping effect of Li to Na_2ZrO_3 was investigated. The change in sorption/regeneration kinetics was evident from the experimental data. The greater the Li content, the lower the CO_2 sorption kinetics. This observation can be attributed to the fact that Li substitutes some of the Na in the Na_2ZrO_3 structure and results in the formation of small amount of Li_2ZrO_3 [60]. Lopez-Ortiz et al. concluded that the highest activity toward CO_2 sorption was exhibited by Na_2ZrO_3, followed by sodium antimoniate (Na_3SbO_4) and finally sodium titanate (Na_2TiO_3). Other applications for Na_2ZrO_3 may involve its use for the development of inorganic membranes for CO_2 separations [24, 61].

Sodium metasilicate (Na_2SiO_3)

Sodium metasilicate has not yet been extensively examined. One of the first studies illustrates the synthesis of Na_2SiO_3 using solid-state and precipitation methods [62]. It was noticed that Na_2SiO_3 can absorb only a small quantity ($\sim$1–2 wt%) of CO_2 in the range of room temperature and 130 °C. Further, the kinetic analysis of CO_2 absorption was also performed, and the results indicate that the sorption mechanism proceeds through a two-step process: (1) superficial chemical sorption and (2) sodium diffusion process. The calculated activation energies for surface reaction and sodium diffusion were 17.48 and 23.97 kJ/mol, respectively. The sodium diffusion is recognized as the limiting step for the carbonation process. Moreover, the CO_2 absorption increases with the decrease in the particle size of Na_2SiO_3 and can be attributed to the subsequent increase in the surface area.

Another study was performed at much lower temperatures (30–60 °C) for the Na_2SiO_3–CO_2–H_2O system [63]. Na_2SiO_3 was synthesized using two methods—(1) solid-state reaction ($Na_2CO_3 + SiO_2$); and (2) combustion method (NaOH, SiO_2 and urea ($CO(NH_2)_2$). The reactions were performed under the flow of two different carrier gasses—N_2 and CO_2. In the presence of N_2 as a carrier gas, Na_2SiO_3 traps water physically and chemically, where the water vapor adsorption and/or absorption depend on temperature and relative humidity. When CO_2 was used as the carrier gas, Na_2SiO_3 traps both water vapor and CO_2. Interestingly, the presence of water vapor promotes the higher CO_2 chemisorption (>1 wt%). It can be seen in reaction series (5) that at first, Na_2SiO_3 reacts with water superficially, producing Na–OH and Si–OH species. Further, superficially activated Na_2SiO_3 combines with CO_2 to form $NaHCO_3$.

$$Na_2SiO_3 \xrightarrow{H_2O} Na_2SiO_{3\,\text{superficially activated}} \xrightarrow{CO_2} Na_2CO_3 + SiO_2 \xrightarrow{CO_2+H_2O} NaHCO_3 + SiO_2 \quad (5)$$

It has also been observed that under the condition of thermal humidity, Na_2SiO_3 absorbs up to 16.39 mmol of CO_2/gm of ceramic, twice more CO_2 than the quantity absorbed under dry conditions. The synthesis method of Na_2SiO_3 influences its CO_2 capture capacity. Higher the surface area, the better is the CO_2 absorption. Here, the surface areas were 0.5 and 1.6 m^2/g for solid-state and combustion method, respectively. Hence, the latter has about 8.6 mmol/g CO_2 capture efficiency, almost twice of that of the former sample. Thus, CO_2 absorption capacity of Na_2SiO_3 is governed by the combined effect of water vapor and surface area. These recent results support the potential of Na_2SiO_3 as a CO_2 capture sorbents at moderate or environmental temperatures.

Table 1 CO_2 uptake capacity of MgO at different conditions

	Sorbent	Gas stream	Carbonation temperature (°C)	Pressure (bar) or flow rate	Particle size	Regeneration temperature (°C)	CO_2 capture capacity (mmol/g) conversion (%)	References
1	MgO	Pure CO_2	50–1,000	100 mL/min (flow rate)	–	–	0.99	[66]
2	MgO/Al_2O_3 (10 wt% MgO)	(13 v % H_2O, 13v % CO_2)	30,150	1	(20–40) mesh size	350	1.36	[67]
3	MgO	(11 v % H_2O, 1v % CO_2)	50–100	0.01	–	150–400	1.05	[68]
4	K_2CO_3/MgO	(11 v % H_2O, 1 v % CO_2)	50–100	–	–	150–400	2.98	[56]
5	MgO	330/660 ppm in air	0,100	0.2	–	–	0.64,0.43	[56, 69]
6	MgO/MCM-41	Pure CO_2	25	1	–	–	1.06	[64]
7	Mesoporous MgO	Pure CO_2	25,100	1	–	–	1.82,2.27	[70]
8	Non-porous MgO	Pure CO_2	25	1	–	–	0.45	[70]
9	$MgO–ZrO_2$	Pure CO_2	30,150	1	–	–	1.15,1.01	[71, 72]
10	MgO (31.7 wt%)/Al_2O_3 (22.4 wt%)	Pure CO_2	20,200,300	1	–	–	0.13,0.24,0.5	[73]
11	MgO (33.8 wt%)/Al_2O_3 (20.8 wt%)	Pure CO_2	20,200,300	1	–	–	0.08,0.12,0.5	[73]
12	K_2CO_3/MgO/Al_2O_3	Flue gas	60	1	–	480	2.49	[74]
13	K_2CO_3/MgO	(9 v % H_2O, 1 v % CO_2)	60	40 mL/min (flow rate)	–	400	2.7	[75]
14	MgO nanocrystal	Flue gas	60	25sccm (flow rate)	5 nm	60–600	6.4	[76]
15	MgO	Pure CO_2	350	1.33,3.33	–	–	0.089,0.091	[77]
16	MgO	Pure CO_2	300–500	9–36	<44 μm	–	70–80 % (~200 min)	[78]
17	MgO	Pure CO_2	–	20–40	<44 μm	–	100 % (~120 min)	[79]

Alkali-earth metal oxides

Magnesium oxide (MgO)

MgO combines with CO_2 to form $MgCO_3$. $MgCO_3$ is thermodynamically stable at ambient conditions. A simple calculation shows that to capture 1 ton of CO_2, about 0.92 ton of MgO is required (assuming 100 % conversion). Thus, it is certain that to capture CO_2 using MgO at any power plant site, a large quantity of MgO will be needed. Moreover, the kinetics and recycling efficiency of MgO–CO_2 reaction are also the major issues to use MgO as a sorbent for practical applications. MgO is an attractive candidate for both pre- and post-combustion capture technologies due to its low regenerating temperatures: $T_2 = 287$ °C (post-combustion) and $T_1 = 447$ °C (pre-combustion) [64]. One should note that MgO when recycled between naturally occurring magnesite and dolomite can cause relatively lesser energy and carbon emission penalty, respectively [65].

Many researchers studied the heterogeneous reaction between magnesium species and CO_2 in the presence or absence of H_2O. Although a majority of research was not directly aimed at carbon capture, still the results are valuable additions to the mineral carbonation research. The CO_2 uptake capacity on different MgO sorbents at various conditions is listed in Table 1. Most of the experiments are restricted to low-temperature and ambient or low-pressure conditions. Hence, the reported sorption capacities of CO_2 on MgO are not very high. In contrast, recent work of Highfield et al. reports a conversion of about 70–80 % MgO to $MgCO_3$ in about 2 h with steam pressure between 5 and 10 % of the total pressure 20–40 bar and temperature around 300–350 °C.

One of the key factors in gas–solid reaction is the presence of water. There have been several observations when

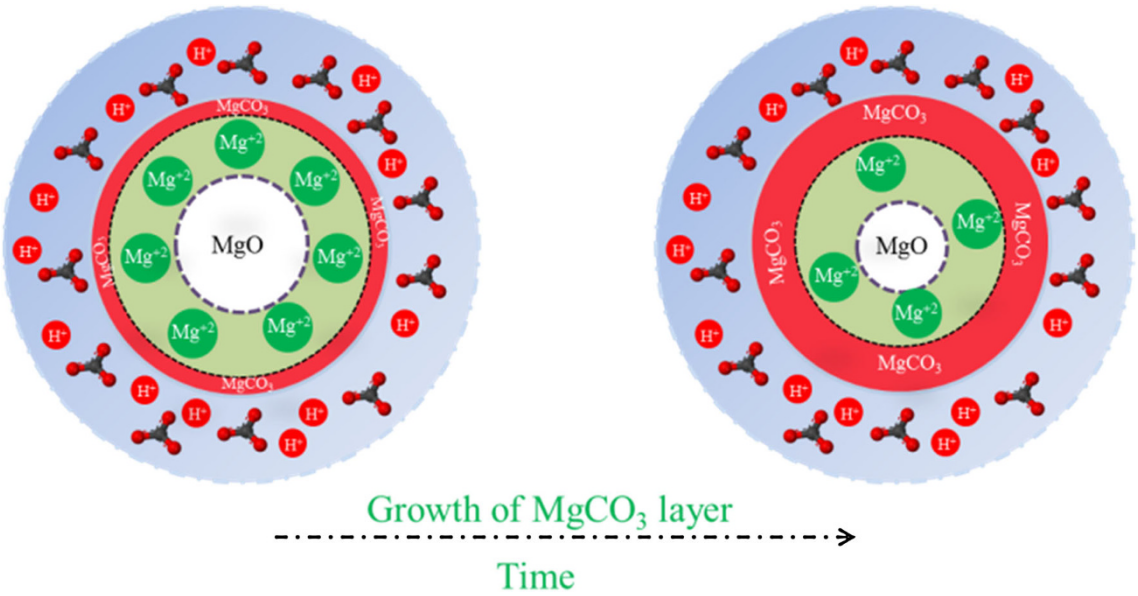

Fig. 5 Adsorption/absorption model for MgO–CO_2–H_2O reaction

water catalyzed the reaction [80, 81]. Figure 5 depicts the absorption/adsorption model of MgO–CO_2–H_2O.

MgO particles are surrounded by water vapor where CO_2 reacts to form CO_3^{2-} ions and H^+ ions. Free Mg^{+2} ions could further react with the CO_3^{2-} ions to form $MgCO_3$. Recently, Fagerlund et al. [78] proposed the reaction mechanism for MgO carbonation in the presence of steam:

$$MgO + H_2O \leftrightarrow MgO \cdot H_2O^* \quad (6)$$

$$MgO \cdot H_2O^* + CO_2 \leftrightarrow MgCO_3 + H_2O \quad (7)$$

$$MgO + CO_2 \leftrightarrow MgCO_3 \quad (8)$$

However, $MgCO_3$ forms an impervious layer around unreacted MgO particles and hinders the further diffusion of CO_2 molecules. Thus, only increasing the amount of water vapor cannot lead to the complete carbonate conversion of MgO. Therefore, besides the amount of steam, surface properties of MgO (such as surface area, particle size and porosity) are also very crucial parameters for the carbonation process. It is observed that in the absence or low partial pressure of water vapor, $MgO{\cdot}2MgCO_3$ is formed. It can be easily calculated that the CO_2 capture capacity of $MgO{\cdot}2MgCO_3$ is about two-thirds that of $MgCO_3$. Hence, formation of $MgO{\cdot}2MgCO_3$ can significantly reduce the further uptake of CO_2 by MgO particles. But at a high temperature (>350 °C), $MgO{\cdot}2MgCO_3$ decomposes to MgO.

MgO–CO_2 reaction has been studied to some extent. The role of water vapor in increasing the activity of MgO is now well established. The direct relation of porosity, surface area and particle size with the carbonation yield has been examined. However, several factors such as carbonation kinetics, sorbent reversibility and durability are still not completely resolved and thus need to be investigated.

Calcium oxide (CaO)

In 1995, Silaban and Harrison proposed the method that involves the separation of CO_2 at high temperatures (>600 °C) using the reversible reaction of CaO [82].

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3(g) \quad (9)$$

The low price (because of naturally occurring mineral, limestone) and favorable thermodynamics of CaO have attracted a lot of interest in the past one decade, and thus, the CaO–CO_2 system has been extensively studied. A great advantage of calcium-based sorbents is that the absorption of CO_2 can occur at temperatures above 600 °C (possibility of heat recovery) [83]. The efficiency of the CO_2 capture depends on many parameters such as diffusion resistance, which depends on the size of sorbent particles, volume and the pore structure, as well as surface size and reaction kinetics [84]. These parameters influence carbonation, but many of them also affect calcination. A detailed list of recent methods used to enhance the CO_2 uptake by CaO-based sorbents can be found elsewhere [85].

Bulk CaO, as a CO_2 sorbent, has three severe limitations: (1) kinetics of the carbonation reaction, despite being highly exothermic, becomes slow after the first layer of carbonate formation because the reaction is limited by the diffusion of CO_2 through the thin surface layer of $CaCO_3$ formed on CaO [86, 87]. The uptake kinetics of CaO-based sorbents was improved by innovative synthesis methods or

precursors [88, 89]. (2) Regeneration step is very energy intensive (>800°C for $CaCO_3$ decomposition), so excessive sintering and mechanical failure of the oxide occur. This leads to a drastic loss in adsorption activity after a few sorption and regeneration cycles [90]. (3) To be an effective sorbent, CaO, that is suitable for high surface area exposure, such as a powder. However, powders can be used in fluidized beds but the pressure drop associated with them is very large. Also, use of fine powders can be problematic due to entrainment in the process flow and attrition of the material [91].

The improvement in the sorbent reversibility can be seen as a major challenge for extended operation purpose. Decrease in absorption capacity is associated with sintering of the sorbent surface because of the influence of temperature and the reduction in porosity and active surface [92–95]. Other factors that reduce the activity of sorbents are the attrition of sorbent grains during the process and chemical inactivation [96]. It should be noted that the reaction with sulfur oxide (SO_2) is competitive to the carbonation reaction. Sulfurization and carbonation reactions are similar because of being heterogeneous and occurring in the porous structure of the sorbent. However, sulfurization is irreversible in the temperature range 500–900 °C, occurs in small pores and covers the surface of the sorbent [97–100]. Decrease in the absorption capacity after 45 cycles was 60 % for limestone, 40 % for dolomite and less than 20 % for huntite, and can be attributed to the differences in the sorbent structure [101]. The decrease in absorption capacity by CaO can be limited in several ways. The parameters that have impact are dopant (NaCl, Na_2CO_3, KCl, $KMnO_4$, $MgCl_2$, $CaCl_2$, Mg $(NO_3)_2$), sorbent grain size, raw material for calcium-based sorbent, thermal pretreatment of the sorbent and steam reactivation. The properties of CaO obtained from calcium acetate are better than the properties of CaO obtained from natural limestone because it has a much better conversion and greater durability [102].

Calcium silicate ($CaSiO_3$)

Calcium silicate received attention because it is inexpensive and has lower sorption temperature compared to CaO. Wang et al. [103] explored the sorption–desorption property of $CaSiO_3$. $CaSiO_3$ is synthesized through solid chemical reaction of $CaCO_3$ and SiO_2 at 800 °C. $CaSiO_3$ starts to absorb CO_2 at 400 °C with about 28.72 % sorption efficiency, using 15 % CO_2 and rest N_2. The observed regeneration temperature for $CaSiO_3$ was 800 °C. However, the CO_2 capture capacity drastically decreases from large number of cycles and could be attributed to sintering of the materials which leads to the loss of specific surface area. Similarly, Gupta and Fan reported that $CaSiO_3$ captured 27.85 % CO_2 at 700 °C and 1 atm [104]. Under the same conditions, Tilekar et al. reported the CO_2 capture capacity of $CaSiO_3$ to be 14.19 wt% [105]. The water molecules in the $CaSiO_3$ facilitate the capture of CO_2.

Transition metal-based oxides

Transition metal-based oxides act as an oxygen carrier in the chemical looping process. In 1983, Richter and Knoche introduced chemical looping for heat generation using metal oxides as chemical ingredients, which are now considered as a potential solution for the simultaneous power generation and CO_2 capture [106]. Metal oxide (Me_xO_y) is reduced by the carbonaceous fuel to generate CO_2 and/or H_2O in the fuel reactor. The reduced metal (Me_xO_{y-1}) is then oxidized back to Me_xO_y by oxygen in the air reactor, which is an exothermic reaction. In the process, transition metal oxides (oxygen carriers) are transported within and between the fuel reactor and the air reactor.

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow n\,CO_2 + mH_2O + (2n+m)Me_xO_{y-1} \quad (10)$$

$$2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y \quad (11)$$

The widely developed oxygen carriers include Ni-, Cu- and Fe-based metal oxides and their composited particles. Despite the great reactivity of Ni- or Cu-based oxygen carriers, their development is restricted because of their relatively high cost. Fe-based oxides are the strong candidates to be commercialized because of their economic feasibility. A number of reviews about the current status of the chemical looping process have been published in recent times [107–111]. Here, the focus is on the direct interaction of CO_2 with transition metal-based oxides via carbonation–calcination cycle.

Iron-based oxides

Iron oxide-based materials can be used for CO_2 capture purpose in both the power and non-power sectors. The main advantages of iron-based sorbent are as follows: (1) accessibility, (2) favorable thermodynamics and (3) slow degradation of sorption capacity.

Recently, Ohio State University developed an iron oxide-based oxygen carrier for particles suitable for operation in the coal direct chemical looping (CDCL) process. CDCL is an efficient power generation process. The process consists of a unique moving bed reactor, namely the reducer, where pulverized coal is fully converted using iron oxide.

$$Fe_2O_3(s) + C(s) \rightarrow FeO(s) + Fe(s) + CO_2(g) \quad (12)$$

$$2FeO(s) + 0.5O_2(g) \rightarrow Fe_2O_3(s) \quad (13)$$

Fe_2O_3, an oxygen carrier, is reduced to FeO and Fe while the exhaust gas is a stream of pure CO_2 that can be sequestered or used for enhanced oil recovery [eq. (12)]. The reduced FeO and Fe mixture can then be oxidized to Fe_2O_3 using air in the combustor reactor, liberating heat to produce steam [112]. Another recent study presents the CO_2 capture technique for iron and steel industries using iron-based raw materials easily available at the iron-making sites [113].

$$Fe_3O_4(s) + Fe(s) + 4CO_2(g) \rightarrow 4FeCO_3(s) \quad (14)$$

$$3FeCO_3(s) + 0.5O_2(g) \rightarrow Fe_3O_4(s) + 3CO_2(g) \quad (15)$$

The global steel production is growing rapidly, from 1,248 Mt in 2006 to 1,490 Mt in 2011—an increase of about 16 % in a short span of 5 years [114]. Steel production is an energy intensive process and thus consumes huge amount of fossil fuels. On world average, each ton of steel production emits 2.2 ton of CO_2. Therefore, iron-making industry is one of the biggest targets next to power plants to curb vast emission of greenhouse gasses.

A mixture of magnetite and iron combines with CO_2 and forms siderite. The reaction generates heat and thus can be utilized to produce steam. Siderite once formed can further decompose back to magnetite in the presence of oxygen at 350 °C. Once the absorption capacity of magnetite degrades, it can be sent back to blast furnace for further processing. For example, the sorbents can be processed in a blast furnace for the production of iron or steel. Thus, the proposed method can advantageously reduce or even eliminate the loss of raw materials. This system and method can be more thermodynamically favorable and can save energy. The reversibility and suitable kinetics can make the system highly favorable for CO_2 capture for iron and steel industries.

Other transition metal oxides

It is considered that MnO can be used for both post- and pre-combustion conditions. At $P_{CO_2} = 0.1$ bar, the driving force for MnO to convert in $MnCO_3$ was high even at a low temperature 77 °C. The CO_2 could be released at about 377°C at partial $P_{CO_2} = 10$ bar. For pre-combustion, MnO will capture CO_2 at a partial pressure of about 10 bar below 327 °C and then could be regenerated by heating above 377 °C to produce a stream of pure CO_2. According to the thermodynamics, CdO can be used for both pre- and post-combustion conditions. However, the toxicity of Cd system would be a big hurdle in its practical applications.

ZnO can be used for post-combustion but not for pre-combustion. The equilibrium temperature required for carbonate formation is 77 °C at $P_{CO_2} = 0.1$ bar and around 167 °C for $P_{CO_2} = 10$ bars [18]. Therefore, it may be essential to cool post-combustion gasses prior to carbonation for high driving force and thus make the sorbent unfit for post-combustion capture. Few researcher groups studied the heterogeneous reaction between ZnO and CO_2 in the presence or absence of H_2O under mild conditions. Previous experiments were performed under mild conditions, mainly room temperature and P_{CO_2} varied from 0.01 atmospheres to 1 atmosphere (atm) [115–117]. Basic zinc carbonate with chemical formula $Zn_3CO_3(OH)_4{\cdot}2H_2O$ was reported as a predominant phase at these conditions. Chen et al. synthesized the compound, zinc carbonate hydroxide hydrate (JCPDS #11-0287), using chemical precipitation method [5.0 % Na_2CO_3 (aq.) added to 0.1 mol/L $ZnSO_4$(aq.)] [118]. A direct relation of heating rate of the sample to its decomposition temperature was noticed. Interestingly, only one endothermic peak for zinc carbonate hydroxide hydrate was observed and was thus attributed to the combined evolution of water vapor and CO_2. The decomposition temperature was observed in the range of 197–257 °C for various heating rate (5–20 °C/min).

$$Zn_4(CO_3)(OH)_6{\cdot}H_2O(s) \rightarrow 4ZnO(s) + CO_2(g)\uparrow + 4H_2O(g)\uparrow \quad (16)$$

ZnO–CO_2–H_2O process is favored by low operating and regeneration temperature and could be ideal for post-combustion CO_2 capture. However, its application is limited due to its rare occurrence in the nature, and this could be the reason for the sparse study of ZnO–CO_2 system.

Similarly, NiO can be considered for post-combustion capture, but not for pre-combustion capture. According to thermodynamics, post-combustion absorption will occur below 77 °C and NiO could be regenerated above 187 °C. However, NiO availability is still a significant concern for its practical application. Therefore, the catalytic potential of NiO leads to its huge application in the CO_2 utilization field. Under sunlight, CO_2 can be converted into methanol in the presence of NiO/$lnTaO_4$ [119–121].

Perovskites

Perovskites have a stable structural framework, despite the movement of active ions into and out of the structure. Such materials have the potential to obviate the challenges associated with the other oxides. Currently, the main issues that most of the oxides face are as follows: (1) rapid degradation of their CO_2 capture capacity over repeated cycles and (2) a large volume change when oxide is converted into

carbonate. Recent reported experimental results have substantially attracted the interest toward perovskites, as potential CO_2 capture materials.

One such study by Galven et al. investigates the CO_2 adsorption behavior of $Li_2SrTa_2O_7$, a layered perovskite family of the Ruddlesden–Popper (RP) phase (general formula, $A_{n-1}\,A'_2\,B_nX_{3n+1}$, where A, A' and B are cations, X is an anion, and n is the number of the layers of octahedra in the perovskite-like stack) [122]. Under humid CO_2 environment, $Li_2SrTa_2O_7$ is transformed into $LiHSrTa_2O_7$ releasing LiOH, which then locks CO_2 in the form of Li_2CO_3.

$$Li_2SrTa_2O_7 + 1/2H_2O + 1/2CO_2 \leftrightarrow LiHSrTa_2O_7 + 1/2Li_2CO_3 \quad (17)$$

It is interesting to note that the operating temperature of $Li_2SrTa_2O_7$ is 140 °C compared to ~400 °C of most of the other inorganic solid compounds. On heating, $Li_2SrTa_2O_7$ can be fully recovered at increased temperature (~700 °C) showing that the CO_2 capture is reversible and can be performed for a number of cycles. Similar CO_2 absorption capacity was observed for $Li_2SrNb_2O_7$. These materials, $Li_2SrTa_2O_7$ and $Li_2SrNb_2O_7$, have phases consisting of layers of corner-connected TaO_6 or NbO_6 octahedra separated by a layer of corner-connected LiO_4 tetrahedra [123]. In the presence of water at room temperature, H^+ shifts Li^+ in the layered structure and allows the shifted Li^+ to react with CO_2 to form Li_2CO_3. During regeneration, Li^+ is reinserted into the Ruddlesden–Popper structure, as in alkali garnet materials [124–127].

Another perovskite material, $Ba_4Sb_2O_9$, can be synthesized using a solid-state reaction in air from $BaCO_3$ and Sb_2O_3 [128]. 6H-$Ba_4Sb_2O_9$ reacts with CO_2 to form $BaSb_2O_6$ and $BaCO_3$.

$$6H\text{-}Ba_4Sb_2O_9 + 3CO_2 \leftrightarrow BaSb_2O_6 + 3BaCO_3 \quad (18)$$

6H-$Ba_4Sb_2O_9$, was found to be able to capture CO_2, mixed with N_2, at 600 °C while the regeneration temperature was around 950 °C under N_2 atmosphere [129]. No significant reduction in the CO_2 absorption capacity was observed for 100 cycles. After 100 cycles, the capacity [~0.1 g (CO_2)/g sorbent] is stable and translates to 73 % of the total molar capacity. The reaction between 6H-$Ba_4Sb_2O_9$ and CO_2 has similar equilibrium constant to that of CaO-based sorbents. However, the CO_2 absorption capacity was stable for a large number of cycles, unlike CaO that degrades rapidly over cycles under same operating conditions.

Miscellaneous

Aluminosilicate zeolite is attractive for post-combustion CO_2 capture due to its selective CO_2 adsorption and high CO_2 capacities [130]. An extensive research has been carried out on aluminosilicate zeolite, and the results exhibit high uptake capacity than pure-silica zeolites [131–133]. In general, adsorption kinetics of CO_2 on zeolites is relatively fast and can achieve equilibrium capacity within a few minutes. The temperature and pressure strongly govern the CO_2 adsorption on zeolites. As the temperature increases, the adsorption of CO_2 decreases but as the gas-phase partial pressure of CO_2 increases, CO_2 adsorption increases accordingly. However, the presence of water vapor may limit the application of zeolite sorbents by decreasing its capacity. It is clear that optimizing different factors, such as basicity, pore size of zeolites and electric field strength (due to the exchangeable cations in the cavities), can significantly influence the CO_2 adsorption capacities of zeolites.

Conclusion

It is certain that an improved and cost-efficient process for CO_2 capture obtained from flue gas streams from power plants burning fossil fuels is needed to mitigate the huge emission of greenhouse gasses. Among several different proposed processes, metal oxides are promising options for suitable sorbent and have a great potential in the future. However, these sorbents also have limitations and challenges which must be solved before these can be employed commercially for CO_2 capture purpose. Based on the current scenario, following suggestions are proposed for the future research on CO_2 capture using metal oxides:

(a) Improvement in the potential sorbent performance, in terms of capture capacity, reversibility rate, carbonation kinetics, multi-cycle durability and sorbent reversibility;
(b) In-depth analysis of performance check of potential sorbent under actual flue gas conditions;
(c) A detailed techno-economic assessment of the potential sorbents;

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